

PRECONTACT SURFACE CHEMISTRY EFFECTS ON CdS/CdTe SOLAR CELL PERFORMANCE AND STABILITY

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ABSTRACT

Carbon-based dag pastes containing mixtures of various Cu-, Sb-, Hg-, and Bi-telluride compounds offer convenient backcontact materials for CdS/CdTe superstrate solar cells. Open-circuit stress tests at 100°C and 1.5 to 2.0 suns illumination show that the performance of devices utilizing Cu-based pastes improves during the first 1-10 hours of stress. Of these, the best stability is exhibited by pastes containing no HgTe. Carbon-based dag pastes can be viewed as sacrificial dopant sources on properly treated CdTe surfaces. CdTe surfaces consisting of thick Te layers, resulting from nitric-phosphoric (NP) acid etches, show better incorporation of active Cu-based dopants than thinner Te layers. Deep-level transient spectroscopy (DLTS) confirms the presence of acceptor-like defects at $\sim E_v+0.3$ eV believed to be associated with Cu_{Cd} substitutional defects in NP-treated devices. The presence of Te and its ability to getter Cu is paralleled by significant improvements in CdTe device stability.

INTRODUCTION

CdS/CdTe devices utilizing Acheson 114 (dag) carbon-based pastes mixed with predetermined amounts of Cu and HgTe compounds have yielded devices with confirmed efficiencies greater than 15% using both SnO_2 [1] and Cd_2SnO_4 [2] transparent conductors on Corning 7059 glass substrates. Both methods utilize a CdS and CdTe layer grown by chemical bath deposition (CBD) and close spaced sublimation (CSS) respectively. CdTe growth is followed by either solution or vapor CdCl_2 treatments (SCC or VCC) at approximately 400°-420°C prior to a standard NP etch (nitric acid to phosphoric acid to water ratio of 1:88:35). Immediately after etching, dag contacts are painted on and annealed at 260°C in He for 25 minutes followed by application of an Ag-paste contact.

Stress test results that show diverging stability behaviors dependent upon load conditions and backcontact composition have stimulated recent developments in CdTe backcontacts[3]. In this paper, we attempt to provide information regarding how device stability is impacted by precontact treatments of the CdTe surface.

EXPERIMENTAL APPROACH

The treatment of CdTe surfaces with NP etchant has been shown to result in the formation of elemental Te surface layers of up to 1 μm thick [4]. The mechanism by which CdTe surfaces are depleted of Cd is described by Sarlund, et al. [5]. In addition to thick layers of elemental Te, NP-etched surfaces are characterized by the presence of TeO_x phases [6]. Similarly, Br:MeOH(BRM)-etched surfaces show Cd-depletion [7], although grazing incidence x-ray diffraction and x-ray photoelectron spectroscopy surface composition measurements by us indicate that the resulting Te layer is significantly thinner, approximately 10-20 Å thick. BRM-etched surfaces, in conjunction with evaporated Cu doping, results in the formation of Cu_xTe prior to device metalization[8]. In our own work using Cu_xTe compounds as the Cu dopant in dag, this compound formation has not been observed at the CdTe surface.

A possible structure for devices that includes the possibility of a "dopant-modified" layer positioned between the Te and dag layers is shown in Figure 1. Also shown is the penetration of the Te-layer down CdTe grain boundaries as reported in ref.[4].

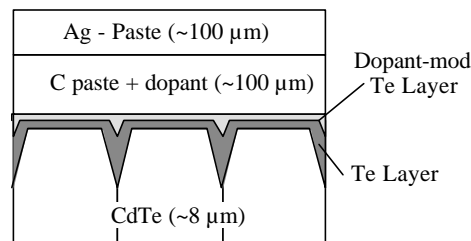


Fig. 1 Layer structure of CdTe/backcontact Interface

Because surface etches with NP and BRM appear to be necessary for making high-efficiency CdTe devices, our initial study was to determine experimentally whether such a modified Te layer existed. For this part of the study, three sets of devices were made: 1) a control group identical to the structure shown above, 2) a set where the dag layer was omitted from the process, and 3) a set where the dag layer was used, then subsequently removed by ultrasonic agitation in methylethylketone (MEK) prior to the Ag-paste contact. To study the effect of Te layer thickness, CdTe films were etched with both NP and BRM prior to contacting.

The second part of this study determined the stability of various carbon-dag pastes mixed with amounts of Cu-, Sb-, Hg-, and Bi-telluride compounds similar to the amounts of Cu found in our original Cu:HgTe dag contacts [1]. Pastes typically consisted of 0.1 to 2.0 g of Cu_xTe ($x=1.4$ or 2.0), Sb_2Te_3 , and Bi_2Te_3 , 0.0 to 2.5 gr of HgTe, and 5 g of Electrodag 114. The starting purity of the Cu_xTe compounds was 99.5%. Higher purities (5N's) were used for the Sb, Bi, and Hg compounds in an attempt to minimize unintentional Cu contamination. Dopant-dag pastes were subsequently cured prior to use. Devices made from these pastes were then stressed at 100°C under open-circuit bias for up to 59 days at ~2 suns illumination.

Finally, we stressed a subset of the devices previously used to show how device series resistance increases with oxygen contamination at the CdTe-backcontact interface [9]. This subset consisted of cells processed with or without the NP etch step. The distribution and activity of Cu in both stressed and unstressed CdS/CdTe cells was compared using secondary ion mass spectroscopy (SIMS) and DLTS.

RESULTS AND DISCUSSION

The "dopant-modified" layer

To determine the existence of the dopant-modified Te layer, we compared devices made with and without a dag layer. In this study, we also used NP and BRM etches. For the latter etchant, we used a low concentration of Br in MeOH (0.5 vol.%) and an etch time of 1 s to minimize previous reports of deep Br penetration effects [7].

The primary results of this study are shown in Figure 2. Curves (1) and (2) show the current-voltage (I-V) response of both a NP and BRM etched control set. These devices represent a "control" process consisting of etching followed by dag+dopant ($\text{Cu}_{1.4}\text{Te}$) application, a 260°C anneal in He, and finally, application of a Ag-paste contact and final 100°C air anneal. It should be noted that each device was replicated twice with excellent reproducibility of the results shown in Figure 2. Curves (3) and (4) represent devices (NP and BRM etched respectively) where the dag step was absent, i.e., after etching, and were only processed with a Ag-paste backcontact. By doing this, our intent was to make devices without the "dopant-modified" Te layer shown in Figure 1. Finally, curves (5) and (6) represent devices (NP and BRM etched) where the dag+dopant was included in the processing, but subsequently removed by MEK ultrasonic agitation prior to the Ag-paste contact.

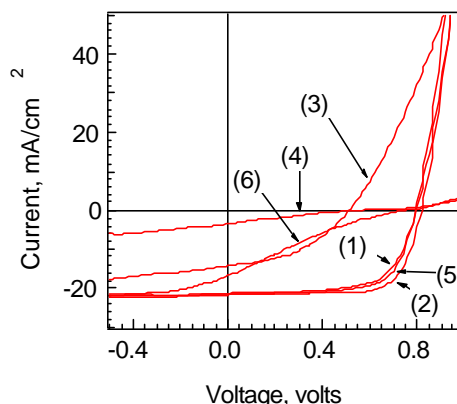


Fig. 2. I-V Light Data. Case (1),(2) std. Dag contact (NP and BRM etches); Case (3),(4) etch without dag; Case (5),(6) etch followed by dag, then dag removal.

The performance of devices with only the Te layer present for both the NP-etched (3) and BRM-etched (4) cases was very poor. When the BRM-etched Te layer was followed by a dag+dopant layer, which was subsequently removed (6), performance improved only slightly. However, the same technique of applying then removing the dag+dopant layer prior to the Ag-paste contact resulted in performance similar to the "control" cases when a NP etchant was used.

Te-rich surfaces should favor the formation of Cd vacancies (acceptors) and Te antisite (donor) states[10]. Both types are reportedly deep-level defects. Though shallow-level acceptors can be expected from complexes between Cd vacancies and Cl substitutional defects [11], this possibility is lessened by the fact NP etches greatly reduce Cl levels at the dag/CdTe interface[9]. The formation of Cd vacancies (and consequently, shallower Cu_{Cd} acceptors) in the CdTe near the Te layer may be favored more so with thick Te layers (NP etched) versus thin Te layers (BRM etched) in much the same way that the solubility of Cd vacancies increase with decreasing Cd overpressure [10]. This may be one possible explanation for why the dag removal technique works so well for NP etched CdTe surfaces, but not for BRM etched surfaces.

Stability of Various Dag-based Contacts

The stability of various dag-based contacts under open-circuit bias held at 100°C under ~ 2 suns illumination is shown in Figure 3, which plots the % change in total-area efficiency versus stress time. In this set of devices, all Cu-containing contacts, the "dag only", HgTe, and Bi-based contact used a NP etch. The Sb_2Te_3 contact required a BRM etch to achieve initial good performance.

Several observations are apparent. First, when considering dag mixtures utilizing Cu as one of the constituents, slight improvements in performance (5%-7%) associated with increased voltage and fill factor were recorded during the first 1-2 days of stress testing. Of this set, the most stable contact after 1000 hours of stress was the $\text{Cu}_{1.4}\text{Te}$ dag contact containing no HgTe. Degradation in

Cu-containing contacts was evidenced by the onset of forward current blocking behavior within the first 1-2 days of stress testing. This roll-over behavior has been attributed to the formation of a reverse-biased diode at the dag/CdTe interface [12].

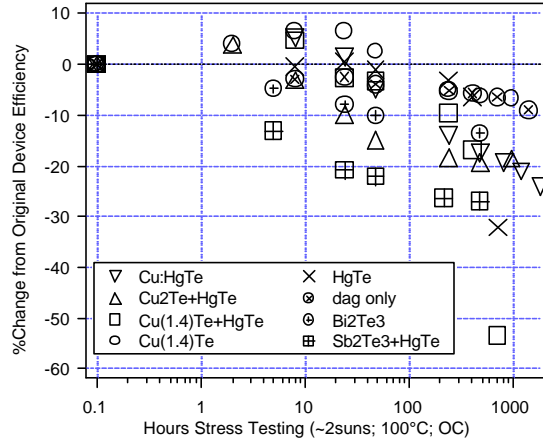


Fig. 3. Dag-paste contact stress data

Also shown in this figure are some initial attempts to duplicate the approach by Romeo, et al. [13] who report excellent stability of sputtered Sb_2Te_3 contacts. When applied using a dag-paste neither this material nor Bi_2Te_3 showed good stability. It should be noted that stress tests like those shown in Figure 3 represent accelerated conditions. Similar tests performed at the max power point are estimated to accelerate in-field degradation by a 10^3 factor[3].

The impact of Te on Device Reliability

In this final part of our paper, we attempt to show how the chemical nature of the Te layer impacts device stability. A previous study [9] had supplied us with a good number of cells where the dag/CdTe interface chemistry included Te-rich, highly oxidized, and near-stoichiometric but possibly Cd-rich surfaces. In this study, it was determined that NP etched surfaces yielded similar device performance regardless of whether SCC or VCC processes were used. However, when considering a process void of any solution etching prior to contacting (and therefore a more manufacturable approach), VCC-treated CdTe surfaces contained much less oxide than SCC-treated surfaces and produced better devices. To evaluate the reliability of non-etched devices and devices with various degrees of oxide at the dag/CdTe interface, we subjected a subset, including both SCC- and VCC-treated films with and without the NP etch, to stress testing. In addition, one device for each process modification was set aside for comparison as an "unstressed" sample.

The results of stress testing (again under open-circuit conditions and 1.5 to 2.0 suns illumination at 100°C) up to 504 hours is shown in Figure 4. In this figure, we show the actual change in measured open-circuit voltage (V_{oc}) and fill factor (FF).

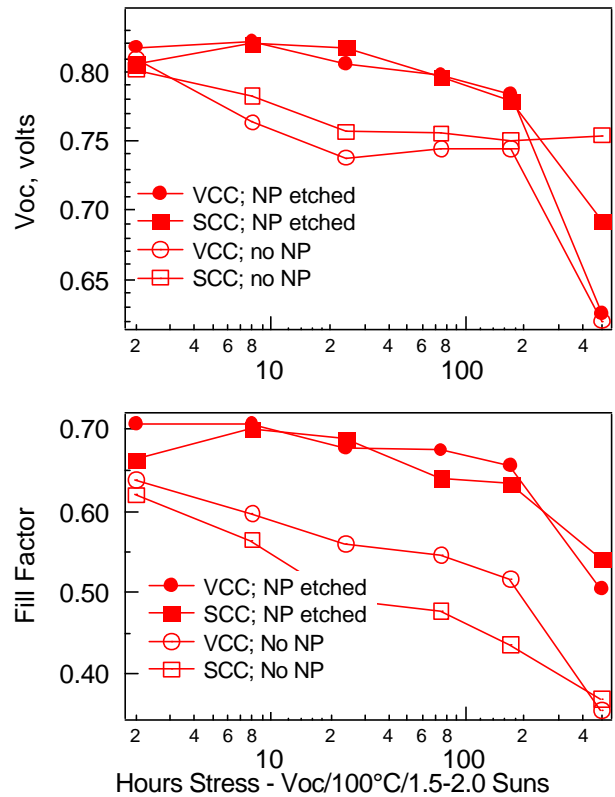


Fig.4. Divergence of stress stability of NP and non-etched CdTe devices

It is obvious that a strong divergence in the performance of cells that have been NP etched and those void of the etch exists. Another observation concerned how the I-V curves of these two groups of cells changed with stress. As mentioned previously, Cu-containing contacts, in conjunction with NP-etched CdTe surfaces, show roll-over within the first 1-3 days of stress testing. During this initial phase, overall performance increases slightly. This behavior was replicated in the devices shown in Figure 4. The non-etched group, however, did not exhibit this behavior. Particularly interesting was the behavior observed with the VCC-treated cells minus the NP etch. In this case, degradation occurs from the onset of stress testing, principally by a rapid decrease in V_{oc} . Roll-over was not observed in this case. We have also observed this switch of the primary degradation mode between roll-over and rapid V_{oc} drops in devices with Cu backcontacts using BRM etches.

SIMS depth profiles of Cu as a function of film thickness for etched and non-etched films with and without stress were taken after removing the backcontact. The variation in Cu for VCC-treated films is shown in Figure 5.

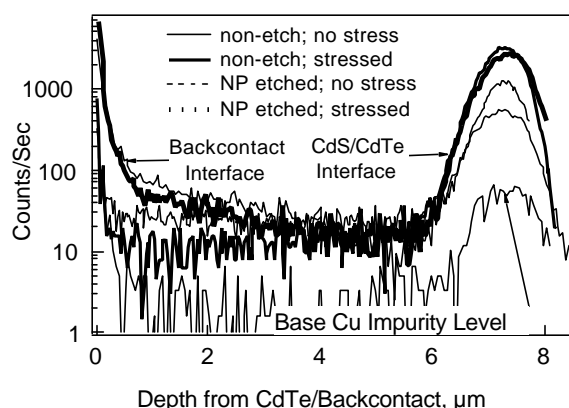


Fig. 5 Cu distribution in NP and no-etched films

Also shown in Figure 5 is the background trace level of Cu impurity measured in our CdTe films before backcontact processing. It is quite clear that films without NP etches contain more Cu at the CdS/CdTe interface before stress than NP-etched films. It is also obvious that Cu segregation at the back is also much greater when NP etches are used. The enhanced degree of Cu at the backcontact/CdTe interface and gradual decrease away from that interface follows the profile of Te (not shown) in these films. In contrast, Cu in non-etched films show much less segregation at the surface and a "flat" distribution in the CdTe bulk again mirroring the Te profile. These results are supportive of Cu gettering by Te.

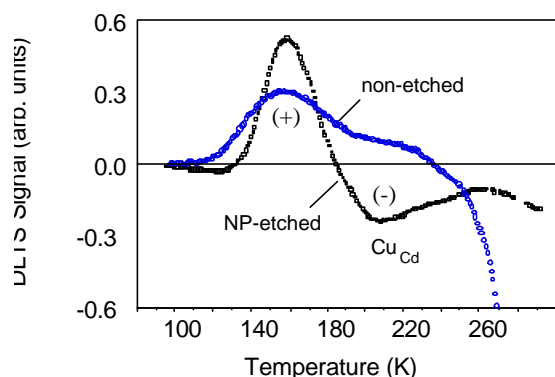


Fig. 6 DLTS difference of NP-etched and non-etched CdTe

DLTS measurements performed between 80-300 K show a distinct difference between NP-etched and non-etched devices (Fig. 6). A recent DLTS study of CSS-grown

CdTe devices using the NP etch identified one dominant electron and two hole traps at $E_c-0.28$ eV, $E_v+0.34$ eV, and $E_v+0.45$ eV respectively[14]. The hole trap at 0.34 eV was believed to be associated with Cu_{Cd} substitutional defects localized in the vicinity of the backcontact. As shown in Figure 6, we have also observed these same defects except for the case of the non-etched devices in which the 0.34 eV states were always absent. This result supports our earlier claim that Te layers, and perhaps the thickness of these layers, play an important role in the ability of Cu to be incorporated as an active dopant near the CdTe/backcontact interface.

SUMMARY

The performance and stability of CdTe solar cells is significantly impacted by the backcontact/CdTe interface chemistry. Elemental Te is observed to impede degradation and favor doping in CdTe through the formation of Cu_{Cd} substitutional defects. Degradation modes are also impacted by whether Te is present or not.

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